Japanese Kokai Patent Application No.: Sho 61[1986]-100530

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KOKAI PATENT APPLICATION NO. SHO 61[1986]-100530

METHOD FOR PARTIAL HYDROGENATION OF POLYCYCLIC AROMATIC COMPOUNDS

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[Attached amendments have been incorporated into the translation.]

Claims

1. Method for partial hydrogenation of polycyclic aromatic compounds, characterized by using catalysts prepared by supporting approximately 10-30 wt% Mo oxide and approximately 1-6 wt% Ni oxide and/or Co oxide on supports, the catalysts having an average pore diameter of approximately 80-180 Å, the range of the pore diameter being within the volume ratio of the following table, and pores with diameter 35 Å or greater having a surface area of approximately 100 m^2/g or greater; the catalysts are used to carry out partial hydrogenation of the 280°C or greater fraction obtained by distillation of coal tar or desludged coal tar, from which light components with lower weight than the absorbing oil fractions were removed, under the conditions of hydrogen pressure 40-180 kg/cm^2G, 300-420°C, and liquid hourly space velocity (LHSV) 0.2-2.0 hr^{-1}, to produce compounds having the factor which indicates the degree of partial hydrogenation derived from ^{1}H-NMR measurement results $0.4 \leq H_\beta/H_\alpha < 1.1$ (wherein H_β is the amount of hydrogen which can be assigned to $\delta = 1.0$-2.0 ppm and H_α is the amount of hydrogen which can be assigned to $\delta = 2.0$-4.2 ppm in the products).

Range of pore diameter	Volume ratio, cc/g
35-50 Å	0.1 or less
50-80 Å	0.3 or less
80-180 Å	0.2-0.5
180-300 Å	0.2 or less
300 Å or greater	0.1 or less

2. Method for partial hydrogenation of polycyclic aromatic compounds described in Claim 1, for producing compounds having the degree of partial hydrogenation $0.4 \leq H_\beta/H_\alpha < 0.78$.

3. Method for partial hydrogenation of polycyclic aromatic compounds described in Claim 1, for producing one compound or at least two compounds from the group consisting of tetrahydroacenaphthene, dihydrophenanthrene, tetrahydrophenanthrene, tetrahydrofluoranthrene, dihydropyrene, and tetrahydrochrysene from an approximately 280°C fraction obtained by

distillation of coal tar or desludged coal tar for removing light components with lower weight than the absorbing oil fractions.

Detailed explanation of the invention

Industrial application field

This invention relates to technology for obtaining partially hydrogenated compounds having specific properties by carrying out light hydrogenation of substances obtained from removing light components from coal tar or desludged coal tar using restricted catalysts and conditions.

Prior art

At present, industrially available coal tar is produced as a by-product at the time of manufacturing coke for iron manufacture, and it is the so-called high-temperature tar. The high-temperature tar is fractionated into light oil (~170°C) which contains BTX and alkylbenzenes, a carbolic oil fraction (170-200°C) which contains phenol, cresol, etc., a naphthalene oil fraction (200-240°C), and an absorbing oil fraction (240-280°C); then each fraction is refined to either obtain the main component as a single substance or as a mixture, and then they are used for various purposes.

On the other hand, a mostly high-boiling-point (280°C or higher) fraction as a soft pitch is used as a raw material for manufacturing carbon black, pitch coke, carbon fiber, etc., except in the case that useful substances such as anthracene, acenaphthene, carbazole, etc., are isolated and refined.

Under such conditions, various research and development has been continuously carried out on the effective utilization of high-boiling-point fractions in coal tar. For example in Japanese Kokai Patent Application No: Sho 51[1976]-136704, a method was disclosed in which at least 50% of raw material oil containing at least 0.5 wt% nitrogen, such as coal tar distilled oil, coal-derived liquid, etc., was subjected to hydrodenitrification.

In Japanese Kokai Patent Application No. Sho 57[1982]-198788, a method was disclosed in which tar pitch or petroleum pitch and coal are subjected to solvent extraction or hydrogenation and the thus obtained pitch-like substance containing at least 10 wt% toluene-insoluble matter was hydrogenated using catalysts prepared by supporting hydrogenation active components such as Ni, Mo, etc., on non-acidic porous supports such as magnesium silicate or silica. In this case, we can assume the above-mentioned [sic] toluene-insoluble matter and quinoline-insoluble matter are hydrogenated and become smaller molecules.

Furthermore in Japanese Kokoku Patent Nos. Sho 49[1974]-11602 and Sho 51[1976]-41129 and Japanese Kokai Patent Application No. Sho 59[1984]-122585, it was disclosed that hydrogenation was carried out for the pretreatment at the time of using tar pitch as

a raw material for coke. In these patents, the first patent describes that the ring of condensed-ring compounds in tar pitch was partially converted to an alkyl side chain; the second patent describes that tar pitch was alkylated first, followed by hydrogenolysis to carry out modification, and the third patent describes a method for obtaining good-quality needle coke from coal tar raw materials.

In addition to these methods, a greater part of the technology in hydrogenation of coal tar pitch including coal-derived liquid was either increasing the lighter components by hydrogenolysis or with the object of desulfurization and denitrification, and further increasing the yield of specific components (such as naphthalene, benzene, anthracene, etc.).

Problems to be solved by the invention

This invention differs from the above-mentioned treatment in that coal tar or desludged coal tar from which the light component fraction had been removed is used as a raw material to obtain partially naphthenated polynuclear aromatic condensed-ring compounds which are useful as raw materials for organic synthesis.

Means to solve the problems

That is, this invention relates to a method for partial hydrogenation of polycyclic aromatic compounds, characterized by using catalysts prepared by supporting approximately 10-30 wt% Mo oxide and approximately 1-6 wt% Ni oxide and/or Co oxide on supports, the catalysts having an average pore diameter of approximately 80-180 Å, the range of the pore diameter being within the volume ratio of the following table, and pores with diameter 35 Å or greater having a surface area of approximately 100 m^2/g or greater. The catalysts are used to carry out partial hydrogenation of 280°C or greater fractions obtained by distillation of coal tar or desludged coal tar, from which light components with lower weight than the absorbing oil fractions were removed, under the conditions of hydrogen pressure 40-180 kg/cm^2G, 300-420°C, and liquid hourly space velocity (LHSV) 0.2-2.0 hr^{-1}, to produce compounds having the factor which indicates the degree of partial hydrogenation derived from ^{1}H-NMR measurement results $0.4 \leq H_\beta/H_\alpha < 1.1$ (wherein H_β is the amount of hydrogen which can be assigned to $\delta = 1.0\text{-}2.0$ ppm and H_α is the amount of hydrogen which can be assigned to $\delta = 2.0\text{-}4.2$ ppm in the products).

Range of pore diameter	Volume ratio, cc/g
35-50 Å	0.1 or less
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180-300 Å	0.2 or less
300 Å or greater	0.1 or less

Operation

The compounds to be hydrogenated, which are the object of this invention, contain various polycyclic aromatics and contain heteroatoms such as N, S, and O in the molecules; therefore, we cannot predict unmistakably their reaction mechanism, but we can assume the main reaction is partial naphthenation of condensed aromatic ring shown in the following model.
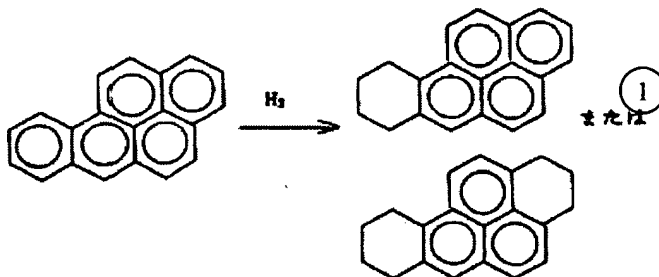
Key: 1 or

All of these formed compounds are practically not contained in the raw materials, and a greater part of them can be formed only under mild hydrogenation conditions.

When oil with high aromaticity, such as soft pitch of coal tar, is hydrogenated, the above-mentioned hydrogenation reaction takes place; however, with the increase in the amount of hydrogen supplied, its aromaticity decreases.

The change of the aromaticity can be calculated quantitatively from ^{1}HNMR spectrum by aromaticity index (f $_a$) which can be defined by the following formula.

$$f_a = \frac{C/H - H\alpha/x - (H\beta - H\gamma)/y}{C/H}$$

wherein C/H is the atomic ratio of carbon to hydrogen in the sample, and x and y which can be considered as the parameters for converting ^{1}H to ^{13}C can be regarded as 2 in this case.

C/H: the atomic ratio of carbon to hydrogen in the sample

H_α :   hydrogen of side chain methyl group at the α-position from the aromatic ring, hydrogen of side chain methylene or methine group at the α-position from the aromatic ring and the hydrogen of naphthene ring at the α-position from the aromatic ring

H_β: hydrogen of side chain methylene group at the β-position or further from the aromatic ring and hydrogen of methylene group and methine group of paraffin,

hydrogen of naphthene compounds and hydrogen of naphthene ring at the β- or further position from the aromatic ring

H$_\gamma$: hydrogen of the side chain at the γ-position or further from the aromatic ring and hydrogen of methyl group at the terminal of paraffin.

One example of the relationship between the amount of hydrogen consumed and f$_a$ is that in the hydrogenation of coal tar soft pitch with f$_a$ = 0.95, if the amount of hydrogen consumed is 500-2000 SCF/bbL, we recognized that the f$_a$ was as low as 0.91-0.70.

In ^{1}H-NMR measurement, carbon disulfide was used as the solvent; the concentration of the sample was adjusted to approximately 3 wt%; tetramethylsilane (TMS) was used as an internal standard substance, and 100% deuterated chloroform was used as a locking agent.

The measurement conditions: at resonance frequency 270.05 MHz, 45° pulse (pulse width 6.8 μsec) was used; the measurements were carried out at 32K data point, observed spectra width 4000 Hz, pulse width 3 sec and integrating frequency 8-10 times.

The various bonded hydrogens in the ^{1}H-NMR spectra were assigned based on the parameter δ value of chemical shift defined by the following formula.

$$\delta \text{ (value)} = (H_r - H_s)/H_r$$

H$_r$ and H$_s$ are the resonance frequencies of the sample and TMS, respectively. δ per se is dimensionless; however, we assume the δ value of TMS be 0, and we express how many parts per million the resonance frequency shifts relatively; thus it is common to express the δ value in terms of ppm.

By using the above-mentioned method, the ^{1}H-NMR spectra of hydrogenated oil of soft pitch was measured, and the results shown in Figure 3 were obtained which, when classified by the aforementioned δ value, obtained the following results.

	δ value (ppm)
H$_\gamma$	0.5-1.0
H$_\beta$	1.0-2.0
H$_\alpha$	2.0-4.2
H$_a$*	6.2-9.2

*: H of aromatic ring.

Of course, from the ratio of the respective area in the ^{1}H-NMR spectra, we can carry out quantitative analysis of the ratio of hydrogen with four bond types.

In carrying out hydrogenation in accordance with this invention, it is necessary to carry out a mild reaction; however, as shown in Figure 2, there is a linear relationship between the degree of partial hydrogenation which can be expressed by H$_\beta$/H$_\alpha$ and the amount of hydrogen consumed at the time of the reaction; thus, it can be adjusted by controlling the amount of hydrogen consumed to 500-2000 SCF/bbL.

It is a matter of course that such a hydrogenation condition does hold good in the presence of specific hydrogenation catalysts, and in this invention, catalysts prepared by supporting Mo and Ni or Co or all three on porous inorganic supports whose main component is alumina or silica/alumina are used. We use the catalysts which contain approximately 10-30 wt% Mo oxide and approximately 1.0-6.0 wt% Ni and/or Co based on the total weight of the catalysts.

For the catalysts, we use those with an average pore diameter of approximately 80-180 Å and the surface area of pores with pore diameter 35 Å or greater is approximately 100 m^2/g.

Range of pore diameter	Volume ratio, cc/g
35-50 Å	0.1 or less
50-80 Å	0.3 or less
80-180 Å	0.2-0.5
180-300 Å	0.2 or less
300 Å or greater	0.1 or less

Basically any of fixed bed, suspension bed, and ebullated bed can be used in the hydrogenation, and it is a matter of course that either a batch or continuous process may be used.

Application examples
Application Example 1

19.8 wt% MoO_3, 4.07 wt% NiO, 0.50 wt% SiO_2, and 1.04 wt% SO_4 were supported on γ-Al_2O_3, followed by molding to a cylinder (1.2.-1.4 mm ϕ x 3.8 mm) (specific surface area 194 m^2/g, pore volume 0.39 cc/g, 50-200-Å pores amounted to 92% of all the pores); then, the cylinder was pretreated for
24 h under the conditions of H_2 140 atm G, 300°C, LHSV 1.0 hr^{-1}, and H_2/oil 1000 NL/L using sulfurized oil prepared by mixing Kafuji gas oil with di-tert-butyl disulfide in such a manner that the S concentration was 1 wt%.

On the other hand, 3% sludge was removed from industrially available coal tar using a known means, and by simple distillation, light components up to 280°C were removed to obtain soft pitch for hydrogenation.

Hydrogenation was carried out using a fixed-bed continuous hydrogenation experimental reactor filled with 200 mL catalyst under the conditions of 360°C, 100 kg/cm^2 G, liquid hourly space velocity 1.0 hr^{-1}, H_2/oil 1000 NL/L, and the amount of hydrogen consumed 1000 SCF/bbL.

The gas by-product was 0.06 wt%; liquid yield was 100.13 wt%; the H_β/H_α of the partially hydrogenated liquid-like matter was 0.65, and the results of GC-MS (gas chromatography-mass spectral analysis) showed that 0.92% (based on the amount fed) of tetrahydroacenaphthene, 1.76% dihydrophenanthrene, 3.37% tetrahydrofluoranthene, 2.01%

tetrahydrophenanthrene, 1.36% tetrahydrochrysene, and 1.16% dihydropyrene were obtained. However, all of these compounds were not in the raw materials (analytical limit 0.01%). These data and data of other application examples and comparative examples are shown in the table to be described later.

This experiment was an experiment in which 50 h elapsed after the start of the reaction. Among the conditions in this example, the results obtained when only the amount of hydrogen consumed was changed and the behavior of the products was measured are shown in Figure 1. The obtention of maximum values shown in Figure 1 was not expected in the past.

Application Example 2

The catalyst used in Application Example 1 was used, and hydrogenation was carried out under the conditions shown in the table to be described later. As a result, the yields shown in the product column were obtained.

Comparative Examples 1 and 2

The catalyst of Application Example 1 was used, and hydrogenation was carried out under the hydrogenation conditions shown. As a result, the yields shown in the product column were obtained.

Application Example 3

20.5 wt% MoO_3, 4.24 wt% NiO, 0.42 wt% SiO_2, and 0.73 wt% SO_4 were supported on γ-Al_2O_3, followed by molding to a cylinder (1.3-1.4 mm ϕ x 3.8 mm) (specific surface area: 144 m^2/g, pore volume: 0.5 cc/g, pore distribution: 100-200 Å pores amounted to 72% of all the pores).

The thus prepared catalyst was used to carry out hydrogenation under the conditions described below, and the yields shown in the product column were obtained.

	Application Example 1	Application Example 2	Comparative Example 1	Comparative Example 2	Application Example 3
Catalyst					
MoO_3 wt%	19.8	19.8	19.8	19.8	20.5
NiO wt%	4.07	4.07	4.07	4.07	4.24
SiO_2 wt%	0.50	0.50	0.50	0.50	0.42
SO_4 %	1.04	1.04	1.04	1.04	0.73
Specific surface area m^2/g	194	194	194	194	144
Pore area cc/g	0.39	0.39	0.39	0.39	0.50

Pretreatment conditions

H_2 atm G	140	140	140	140	140
Temperature °C	300	300	300	300	300
LHSV h^{-1}	1.0	1.0	1.0	1.0	1.0
H_2/oil NL/L	1000	1000	1000	1000	1000
Time h	24	24	24	24	24

Hydrogenation

Amount of catalyst used mL	200	200	200	200	200
Temperature °C	360	360	400	360	360
Pressure kg/cm^2 G	100	50	180	50	140
LHSV h^{-1}	1.0	0.75	0.5	1.67	0.8
H_2/oil ratio NL/L	1000	1000	1000	1000	1000
Amount of H_2 consumed SCF/bbL	1000	690	3250	300	1670
Gas by-product wt%	0.06	0.06	0.84	0.03	0.08
Liquid yield wt%	100.13	100	100.77	100.00	101.62
H_β/H_α	0.65	0.49	1.67	0.31	0.96

Products wt%

Tetrahydroacenaphthene	0.92	0.45	0.14	0.13	2.14
Dihydrophenanthrene	1.76	0.70	0.12	0.24	1.91
Tetrahydrofluoranthrene	3.37	2.14	1.35	0.45	3.17
Tetrahydrophenanthrene	2.01	1.78	0.25	1.21	1.24
Tetrahydrochrysene	1.36	1.07	0.53	0.50	1.26
Dihydropyrene	1.16	0.89	0.72	0.25	1.25

Effect of the invention

The partially naphthenated compounds obtained by this invention have more active hydrogen and alicyclic structures than those of their respective starting materials and are remarkably easier to oxidize and cleaved. Therefore, they are useful as raw materials and intermediates for organic synthesis; concretely when they are isolated, they may be employed as raw materials for medicine, agricultural chemicals, dyes and pigments, special grade polymers, and when they are used as mixtures, they can be employed as raw materials for good-quality carbon black and good-quality needle coke.

The boiling point of the thus obtained partially hydrogenated products is lower than that of their respective starting materials so that we can carry out hydrogenation at the time of isolating the original substances, followed by dehydrogenation to convert them to their original substances.

Brief description of the figures

Figure 1 shows the yield of partially naphthenated products versus the amount of hydrogen consumed.

Figure 2 shows the relationship between the amount of hydrogen consumed and the degree of partial hydrogenation.

Figure 3 shows ^{1}H-NMR spectra.
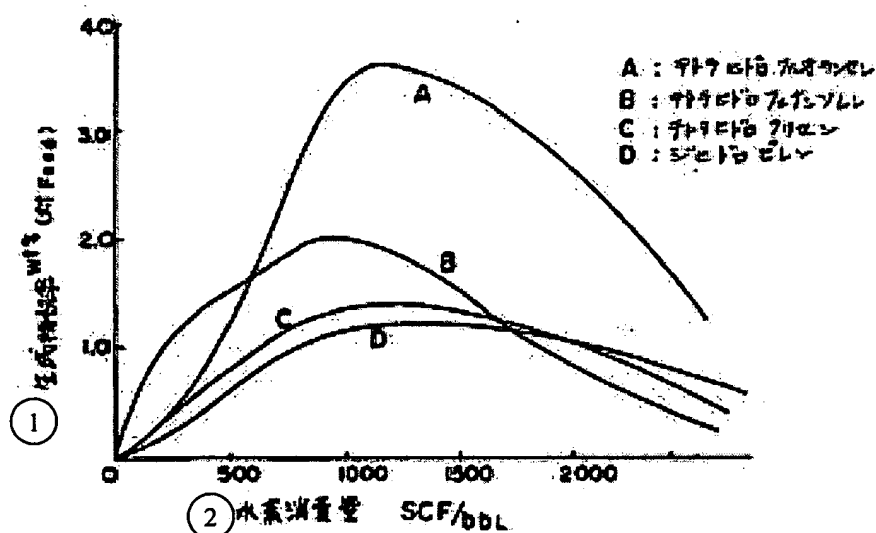

Figure 1

Key: (1) Yield of products, wt% (based on feed)
     (2) Amount of hydrogen consumed
     A: Tetrahydrofluoranthene
     B: Tetrahydrophenanthrene
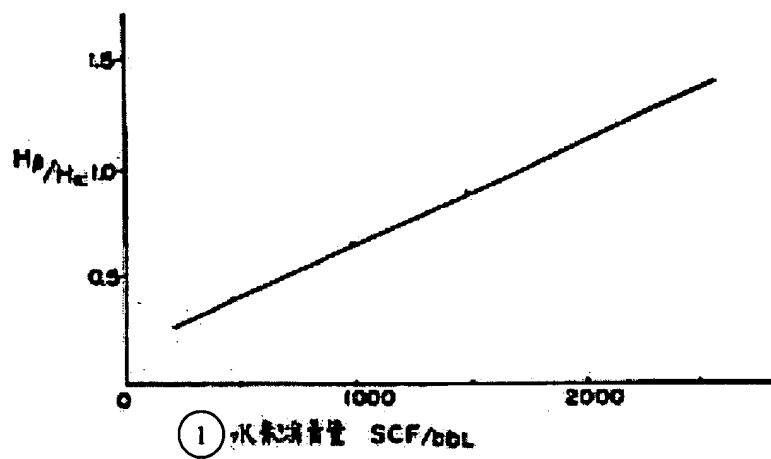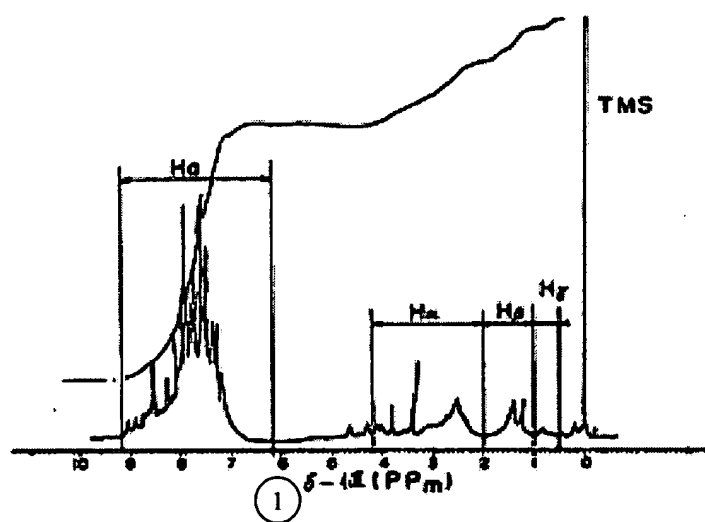   C: Tetrahydrochrysene
     D: Dihydropyrene

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Figure 2

Key:　(1)　Amount of hydrogen consumed

Figure 3

Key:　(1)　δ value